

DRAFT WORK PLAN

MARINA DEL REY HARBOR SITE-SPECIFIC OBJECTIVE STUDY

Prepared for

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LIST OF ACRONYMS AND ABBREVIATIONS

ANOVA	Analysis of Variance
BLM	Biotic Ligand Model
CCC	Criterion Continuous Concentration
CIMP	Coordinated Integrated Monitoring Program
COC	chain-of-custody
CTR	California Toxics Rule
DOC	dissolved organic carbon
DQO	data quality objective
EC50	median effective concentration
fWER	final Water-Effect Ratio
LACDPW	Los Angeles County Department of Public Works
MdR Harbor	Marina del Rey Harbor
µg/L	microgram per liter
mL	milliliter
QA	quality assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
RWQCB	Regional Water Quality Control Board
SSO	site-specific objective
sWER	sample Water-Effect Ratio
SWRCB	State Water Resources Control Board
TAC	Technical Advisory Committee
Toxics TMDL	<i>Reconsideration of the Total Maximum Daily Load for Toxic Pollutants in Marina Del Rey Harbor</i>
USEPA	U.S. Environmental Protection Agency
WER	Water-Effect Ratio

I. INTRODUCTION

The *Reconsideration of the Total Maximum Daily Load for Toxic Pollutants in Marina Del Rey Harbor* (Toxics TMDL; Los Angeles RWQCB/USEPA 2013) includes load allocations for dissolved copper inputs to Marina del Rey Harbor (MdR Harbor). This section provides a brief overview of the regulatory background for MdR Harbor that led to the inclusion of dissolved copper water column targets in the revised Toxics TMDL and discusses the rationale and background for using a site-specific objective (SSO) study to develop a scientifically defensible water quality criterion that accounts for site-specific conditions and focuses on the protection of aquatic life in the MdR Harbor.

Regulatory Background

In 1998, the back basins of MdR Harbor were placed on the 303(d) list for contaminants impacting sediment, fish tissue, and benthic infauna. At this time, pollutants of concern for sediment included DDT, chlordane, lead, copper, and zinc and pollutants of concern for fish tissue included those for sediment and PCBs, dieldrin, and tributyltin (TBT). However, in 2002, changes were made to the 303(d) list; copper, lead, zinc and TBT in fish tissue, DDT in sediment, and benthic infauna degradation were delisted and PCBs in sediment for MdR back basins were newly listed. Based on the 303(d) list and its subsequent modifications, the MdR Harbor Toxics TMDL was promulgated in 2005 to address impairments associated with sediment for copper, lead, zinc, chlordane, PCBs, and toxicity and fish tissue for DDT, dieldrin, chlordane, PCBs, and fish consumption advisory (Los Angeles RWQCB/USEPA 2005). Monitoring and special studies conducted in support of the Toxics TMDL have since provided additional information regarding the spatial extent and magnitude of the impairments; the special studies include partitioning coefficient, a low detection level, storm-borne sediment pilot, sediment characterization and BMP effectiveness studies. The results have shown that dissolved copper concentrations frequently have exceeded the chronic (4-day average) criterion (also referred to as Criterion Continuous Concentration [CCC]) of 3.1 micrograms per liter ($\mu\text{g/L}$), as specified in the California Toxics Rule (CTR).

The Toxics TMDL was revised and adopted by the Los Angeles Regional Water Quality Control Board (RWQCB) in February 2014 (Los Angeles RWQCB 2014) and was subsequently approved by the State Water Resources Control Board (SWRCB) in September of 2014 (SWRCB 2014). Toxics TMDL revisions were designed to take into consideration new data on the spatial extent and magnitude of sediment contamination as well as address the dissolved copper CTR exceedances in the water column. As such, the Toxics TMDL includes load allocations for dissolved copper required to ensure that dissolved copper concentrations in MdR Harbor are less than the CCC criterion in the CTR.

In SWRCB Resolution 2014-0049 (SWRCB 2014), the SWRCB recognizes that the U.S. Environmental Protection Agency (USEPA)-approved Water-Effect Ratio (WER) method may be used to derive site-specific water quality objectives and, if adopted by the Los Angeles RWQCB and approved by the SWRCB Office of Administrative Law and USEPA, will supersede the current CTR CCC criterion as the water quality standard for dissolved copper in Mdr Harbor. Conditional approval to conduct a SSO study for Marina del Rey Harbor was granted by the Los Angeles RWQCB in September 2017 (revised in June 2018).

Development of Site-specific Objectives

Although there are exceedances of the dissolved copper CCC in Mdr Harbor, the concentration threshold necessary to protect aquatic life in Mdr Harbor is uncertain. It is well known that water quality parameters (e.g., pH, dissolved organic carbon [DOC], and salinity) influence the biological availability of copper in marine water and may reduce the potential to cause toxicity to aquatic life (USEPA 1994; Di Toro et al. 2001). In addition, the federal water quality criteria (from which the CTR criteria were derived) for dissolved copper were developed to be conservative in order to be protective of marine aquatic life in all waters of the U.S. regardless of site-specific water characteristics. Specifically, water quality criteria were developed based on laboratory studies in which filtered seawater was used, and consequently, these studies do not necessarily account for many of the physical constituents (e.g., particulate and dissolved organic matter) that may interfere with the toxicity of potential chemicals of concern, such as copper. Consequently, the USEPA has developed procedures that can be performed to develop water quality criteria that are specific and reflective of site-specific conditions, while still providing the required level of protection for aquatic life.

The *Interim Guidance on Determination and Use of Water-Effect Ratios for Metals* (USEPA 1994) provides guidance for determining SSOs. This guidance includes three options: 1) the recalculation procedure; 2) the WER procedure; and 3) the resident species procedure. The recalculation procedure is intended to account for relevant differences between the sensitivities of the aquatic organisms in the national dataset and the sensitivities of organisms that occur at the site. The WER approach compares the toxicity of copper dissolved in different water types to determine an adjustment factor for the water quality standard. The resident species procedure is intended to account for differences in resident species sensitivity to biological availability and/or toxicity of a material due to variability in physical and chemical characteristics of the site water.

The Biotic Ligand Model (BLM) is another USEPA-approved approach for determining site-specific criteria for dissolved metals in freshwater environments (Di Toro et al. 2001; Santore et al. 2001). A marine version of the BLM is currently under review by the USEPA but has not yet

been approved. Nonetheless, some testing in marine environments has been performed to evaluate the BLM's ability to predict toxicity at marine sites throughout the United States (Arnold et al. 2005). Results have shown that the BLM can provide an accurate prediction of copper toxicity to sensitive marine taxa in marine receiving waters and that the BLM-predicted toxicity is strongly correlated with measured toxicity. The BLM approach requires only chemical and physical water quality data as inputs and consequently is a more cost-effective and less time-consuming method than the toxicity-based WER. Because of its efficiency, the BLM may allow for the examination of a wider range of site-specific conditions than could be captured during WER studies as well as evaluation of effectiveness of various management strategies.

In this study, WER procedures that are consistent with the USEPA (1994) Interim Guidance¹ will be used to calculate SSOs for MdR Harbor that are scientifically defensible and protective of beneficial uses. The BLM will be used during the critical condition evaluation to support the determination of environmental conditions likely to result in the lowest SSO; this approach will result in an SSO that is protective of aquatic organisms under all environmental conditions. The BLM will also be used to estimate WERs and SSOs in MdR Harbor for comparative purposes.

1. Water-Effect Ratio

The USEPA recommends calculating a WER to account for site-specific bioavailability and toxicity of contaminants (USEPA 1994). As part of a WER study, two side-by-side toxicity tests are conducted; one test uses laboratory dilution (clean) water and the other test uses site (contaminated) water. The WER is determined by calculating the ratio of the median effective concentration (EC50) values from the two tests as shown in Equation 1:

$$\text{WER} = \frac{\text{EC50 Site water}}{\text{EC50 Control or Reference water}} \quad (1)$$

The WER is then multiplied by the national or state aquatic life criterion; in this study, the CTR CCC (to represent chronic conditions) criterion and criterion maximum concentration (CMC, to represent acute conditions) will be used. Unlike in freshwater, the marine CCC and CMC are not hardness dependent.

¹The USEPA also published a streamlined procedure for the WER development for copper in freshwater (USEPA 2001). The streamlined procedure provides simplified WER testing specific to a waterbody where a continuous point source, such as publically owned treatment works, primarily contributes to an elevated level of copper. The streamlined WER guidance is not applicable to MdR Harbor due to differences in salinity and source of copper.

To calculate SSOs, the WER is multiplied by the water quality criteria as shown in Equation 2:

$$\text{Chronic SSO} = \text{WER} \times \text{CCC} \quad (2)$$

$$\text{Acute SSO} = \text{WER} \times \text{CMC}$$

The WER developed in this study will be appropriate for adjustment of both the CCC and CMC, as both criteria are applied in the TMDL to the same locations within MdR Harbor.

2. Biotic Ligand Model

The BLM is a computational model used to predict metal speciation, complexation, and toxicity to aquatic organisms using site-specific water characteristics (Di Toro et al. 2001; Santore et al. 2001). The BLM was originally designed to estimate copper toxicity in freshwater fish and invertebrates; however, it has been used successfully in estuarine systems as well (Arnold et al. 2005; Chadwick et al. 2008). The BLM is based on the premise that both metal–ligand binding and metal interaction with competing cations may affect toxicity (Di Toro et al. 2001). Thus, the degree of toxicity is expected to be related to the amount of metal available to bind to the biotic ligand, the concentration of other aqueous ligands such as organic matter that can bind up the metal of concern, and the availability of other cations (i.e., calcium), which may have a protective effect.

The marine version of the BLM uses water chemistry inputs (e.g., pH, DOC, temperature, and salinity) to calculate bioavailable metals concentrations in water and metal binding affinity to biotic ligands. The BLM then predicts metal toxicity to aquatic organisms based on these calculations and outputs EC50 values.

A BLM-based WER can be calculated using the BLM-predicted EC50 outputs for both site water and control or reference (clean) water as shown in Equation 3:

$$\text{BLM-based WER} = \frac{\text{BLM-predicted EC50 Site Water}}{\text{BLM-predicted EC50 Control or Reference Water}} \quad (3)$$

BLM-predictive SSOs may then be calculated using Equation 2 in Section 1.2.1.

3. Previous Marine or Estuarine Water-Effect Ratio Studies

While WER studies have been performed in freshwater environments nationwide, only a few WER studies conducted in California marine or estuarine waters are publicly available at this

time. Only two marine/estuarine WER studies in California have resulted in SSOs that were adopted by a RWQCB and approved by the SWRCB. For other studies conducted in the marine environment, the status of adoption by the relevant RWQCB is currently unknown (LWA 2006) or the goal of the study was to better understand bioavailability of copper to aquatic organisms, as in Rosen et al. (1995) and Bosse et al. (2014), but not to develop an SSO. The most relevant studies are summarized below.

1.1.1.1 Lower South San Francisco Bay (South of Dumbarton Bridge)

An impairment assessment study for copper (and nickel) was conducted for Lower South San Francisco Bay (Tetra Tech et al. 2000). WER testing was a key part of this study and was used to understand how site-specific water quality parameters affect the bioavailability and toxicity of dissolved copper within the Lower South San Francisco Bay. The blue mussel *Mytilus edulis* and the purple sea urchin *Strongylocentrotus purpuratus* were used in this testing as primary and secondary species, respectively. Samples were collected from three sites in South San Francisco Bay, and tests were conducted from January 1996 to March 1997 to understand the temporal variability in copper bioavailability of Lower South San Francisco Bay waters. Results of this study demonstrated WER values ranging from 2.7 to 3.5 for dissolved copper. SSOs ranging from 6.7 to 8.8 µg/L for dissolved copper were then calculated using a modified CCC of 2.5 µg/L, based on toxicity test data collected as part of the study. A proposed SSO of 6.9 µg/L was recommended by the City of San Jose, based on pooled WER results from two stations and was suggested to be protective of the most sensitive species, *M. edulis*. An SSO of 6.9 µg/L was adopted by the San Francisco Bay RWQCB in 2002 (San Francisco Bay RWQCB 2002).

1.1.1.2 San Francisco Bay (North of Dumbarton Bridge)

A WER study was conducted in San Francisco Bay in 2000/2001 for purposes of developing copper SSOs for San Francisco Bay regions north of the Dumbarton Bridge (Clean Estuary Partnership 2005; San Francisco Bay RWQCB 2007a). Sampling was conducted at 13 stations that were selected based on stations previously sampled by the Regional Monitoring Program. The study involved sampling and WER testing during two dry seasons (September 2000 and June 2001) and two wet season (January and March 2001) events. Copper toxicity tests were performed using the bivalve *M. edulis* mussel development test. Results did not demonstrate a seasonal pattern in WERs; however, differences in WERs across San Francisco Bay regions were measured and were likely due to differences in the physicochemical characteristics of water from different regions of San Francisco Bay. The geometric mean WERs for the San Francisco Bay regions north of San Bruno Shoal (i.e., north of Oakland airport on the eastern side and north of Little Coyote Point on the western side) ranged from 2.40 to 2.49 and the geometric mean WER for the region south of San Bruno Shoal was 2.90. Based on these findings, the Basin Plan Amendment proposed chronic and acute copper SSOs of 6.0 and 9.4 µg/L, respectively, for the

area north of San Bruno Shoal and chronic and acute copper SSOs of 6.9 and 10.8 µg/L, respectively, for the region south of San Bruno Shoal. These SSOs were adopted by the San Francisco Bay RWQCB in 2007 (San Francisco Bay RWQCB 2007b).

1.1.1.3 San Diego Bay Studies

Rosen et al. (2005) evaluated the bioavailability of copper to organisms in the San Diego Bay. Water samples included composite and grab samples that were collected from various locations inside the bay from 2000 to 2002. Bivalve *Mytilus galloprovincialis* and echinoderm *S. purpuratus* or *Dendraster excentricus* embryos were used in WER toxicity tests. For WER calculations, EC50s from the copper-spiked San Diego Bay water samples (from various areas of the Bay) were compared to those from toxicity tests of copper-spiked reference seawater, which was filtered (0.45 micron) coastal seawater collected from the research pier at Scripps Institute of Oceanography. Estimates of the dissolved copper WER ranged from 1.54 to 1.67. These findings of WERs greater than 1 in San Diego Bay suggest that a SSO ranging from 4.7 to 5.2 µg/L (based on the WER range above) would be protective of the organisms throughout San Diego Bay.

More recently, a study of the bioavailability and toxicity of copper was conducted in Shelter Island Yacht Basin, a marina in North San Diego Bay (Bosse et al. 2014). As part of this study, WER sampling and testing was conducted in conjunction with copper complexation capacity measurements and modeling using the marine BLM. Samples were collected at two depths (near surface and near bottom) during two sampling events, representing the wet season and the dry season. Sampling for ambient toxicity occurred at 15 to 16 stations during each event, and samples from four of these stations were spiked with copper for use in WER testing. *M. galloprovincialis* embryos were used as the test species as part of the standard mussel development test (USEPA 1995). Results of this study demonstrated slightly lower WERs in the wet season (geometric mean of 1.2 ± 0.1) than in the dry season (geometric mean of 1.5 ± 0.2) with a final dissolved copper WER for all events of 1.33. These findings suggest that an SSO of 4.11 µg/L would be protective of marine organisms in the Shelter Island Yacht Basin.

1.1.1.4 Mugu Lagoon and Lower Calleguas Creek, Ventura County

A WER study for copper was conducted for Mugu Lagoon and Lower Calleguas Creek (LWA 2006) in accordance with the USEPA (1994) Interim Guidance. However, only the results for Mugu Lagoon, which is a marine environment, are relevant to the current study and are summarized here. Samples were collected during dry weather conditions in August 2003 and January 2004 and wet weather conditions in March 2004 and April 2006. *M. edulis* were the primary test species, and the larval bivalve development test was used to evaluate copper

toxicity. The recommended WER for dissolved copper in Mugu Lagoon was determined to be 1.51, resulting in a chronic SSO established as 4.68 µg/L (LWA 2006).

1.1.1.5 Summary of Previous Water-Effect Ratio Studies

All studies summarized above have demonstrated WER results that were greater than 1. WER findings from these studies ranged from 1.33 in Shelter Island Yacht Basin to 3.5 in Lower South San Francisco Bay. SSOs estimated from these WER results range from 4.11 to 8.8 µg/L; however, to date, only the San Francisco Bay SSOs (ranging from 6.9 to 10.8 µg/L) have been adopted by the RWQCB (San Francisco Bay RWQCB 2002). These findings demonstrate that at each of these sites, a higher SSO than the current CTR CCC criterion of 3.1 µg/L would be protective of marine aquatic life and beneficial uses of those sites.

Study Objective

The objective of this study is to develop a scientifically defensible SSO for MdR Harbor that accounts for site-specific conditions and is protective of aquatic life and the beneficial uses of MdR Harbor.

II. STUDY DESIGN AND METHODS

This section comprises the WER study design and includes the details of the sampling program, analytical methods, and data analysis. The overall approach is based on the USEPA (1994) Interim Guidance for determining water effects ratios for metals. As stated in this guidance, development of WERs for surface waters (e.g., bays and harbors) located away from effluent plumes is a more complex and variable situation than developing WERs for plume-influenced waters. Consequently, few specific requirements for study design are provided in the USEPA (1994) Interim Guidance; instead, qualitative descriptions and recommendations are provided to guide the investigator in developing the specifics of the study. In addition, relatively little guidance is provided for WER studies in marine waters.

The approach used to develop the MdR Harbor WER study design was to adhere to the conceptual approach described in the USEPA (1994) Interim Guidance and implement this approach by using methods shown to be effective in recent successful California WER studies. Study design and method selection is based on three studies: 1) WER calculation for Los Angeles River and tributaries TMDL (Steering Committee 2014); 2) San Francisco Bay copper and nickel SSO derivation (Clean Estuary Partnership 2005); and 3) studies of copper bioavailability and toxicity in San Diego Bay (Bosse et al. 2014). Two of these studies (Steering Committee 2014 and Clean Estuary Partnership 2005) resulted in SSOs for copper that were adopted by regulatory authorities for use in total maximum daily loads.

The key elements and sequence of the study design are shown in Figure 1 and are described in subsequent subsections. Toxicity testing will be the primary method used to calculate WERs. Thus, selecting test species and the test method is the first step in study design (Section 2.1). In addition, WERs and copper toxicity (EC50) will be predicted for every water sample using the BLM. The predicted WERs will be used to guide the selection of stations for the WER study. In the final phase of the study, both the toxicity and BLM approaches will be used to calculate separate WERs for each sample (sWER).

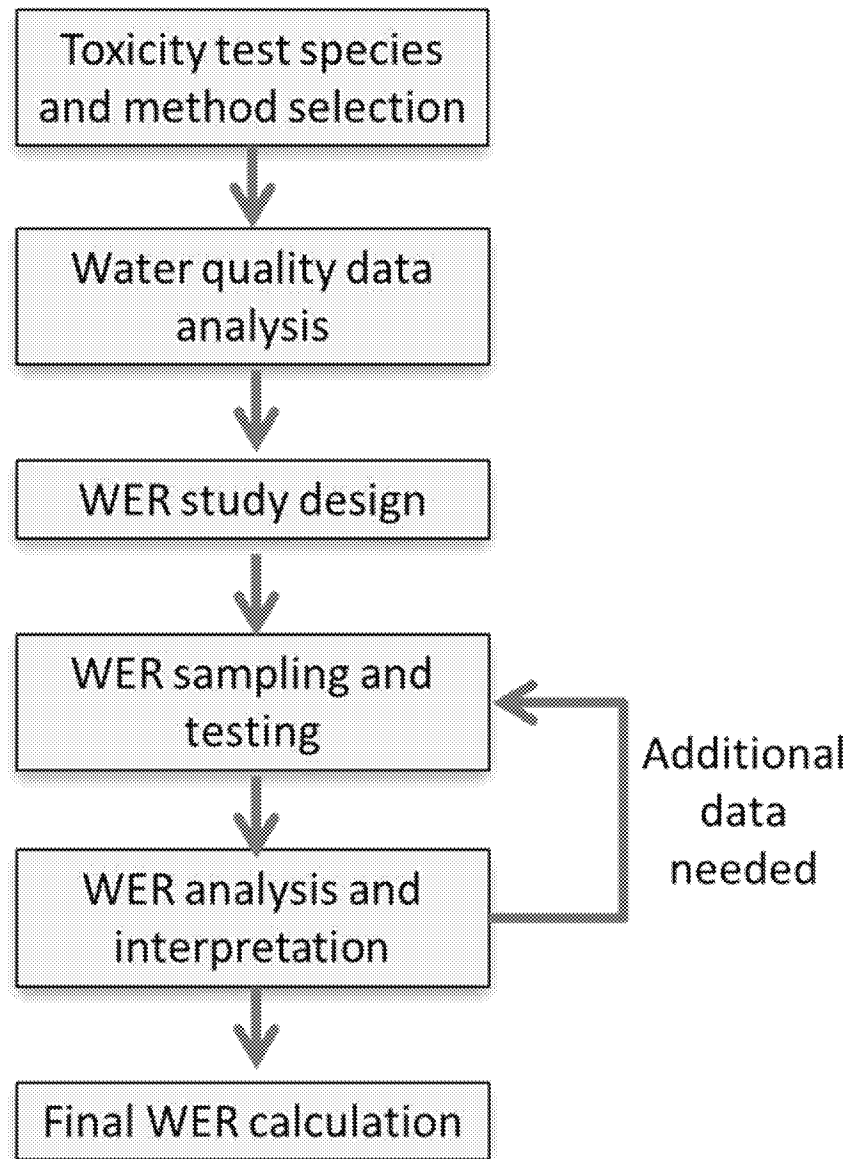


Figure 1. Study elements and process.

The USEPA (1994) Interim Guidance emphasizes the importance of developing a sampling design that considers variations in water quality likely to affect the WER. Potential sources of variability include seasonality (e.g., summer vs. winter), stormwater discharge, hydrology (tides or depth), and episodic events (e.g., plankton blooms and harbor activities). The relative importance of these factors in controlling or influencing bioavailability of copper in MdR Harbor is not known; therefore, preliminary water quality sampling will be conducted to characterize conditions in MdR Harbor and predict variations in copper bioavailability using the BLM.

The results of the water quality analyses will be used to develop the final WER study design (Section 2.2). The final design will emphasize sample collection during the conditions when the WER is expected to be lowest and the risk of copper toxicity is greatest, known as the critical condition. Each water sample will be analyzed to determine the copper toxicity EC50, copper concentration, and BLM parameters (Section 2.2.3), and the results used to calculate the sWER for each sample (Section 2.4). This step will include an assessment to determine if sWER data are sufficient to support the objectives of the study. If deficiencies are present, additional sampling may be needed to resolve them.

The final step in the data analysis is the calculation of the final WER (fWER, Section 2.5). One or several fWERs may be calculated, depending on the results of the study.

Toxicity Test Species and Method Selection

Toxicity tests will be conducted using embryos of the *M. galloprovincialis*. This species is recommended for WER calculation in the USEPA (1994) Interim Guidance and has been the primary or sole species used for WER development in recent studies in San Francisco Bay (San Francisco Bay RWQCB 2007a) and San Diego Bay (Bosse et al. 2014). *M. galloprovincialis* is an almost ideal organism for use in WER copper studies because of its sensitivity to copper and commercial importance. When deriving a site-specific criterion, it is desirable to use a test species that is sensitive at CCC or Criterion Maximum Concentrations. The EC50 for *M. galloprovincialis* embryo development is similar to the criteria concentrations. In addition, use of this species helps provide an additional margin of safety for SSO development for two reasons:

- The current CTR criterion for copper is determined exclusively by *M. galloprovincialis*, for protection of this commercially important species. Because it is used exclusively for setting current criteria, using this species in the MdR Harbor SSO study will help ensure that the same level of protection is maintained.

- *M. galloprovincialis* is the most sensitive species in the national saltwater copper toxicity database. It is not only a good surrogate for invertebrate species (which tend to be more sensitive to copper than vertebrates) and mollusks (a phylum sensitive to copper; the third, fourth, and sixth most sensitive species in the national copper database are mollusks), but it is a good surrogate for other sensitive saltwater aquatic animals.

4. Test Method

Site water and laboratory control seawater toxicity will be measured using a 48-hour exposure of mussel embryos under standard conditions as described USEPA (1995). Test conditions are summarized in Table 1 and detailed methods are described in Appendix A.

Control seawater will be obtained from a reference site in Granite Canyon, California, and filtered (0.45 micron) prior to use to remove resident organisms and particulate organic material. This reference site has been used for control water in previous WER studies in San Francisco Bay and San Diego Bay due to its previously reported acceptability for embryo-larval development tests and relatively low DOC content.

Copper-spiked water samples for WER tests will be prepared by adding reagent grade copper salt solutions. Spiking methods and concentrations will be consistent with the USEPA (1994) Interim Guidance. Both site water and control water samples will be spiked with specific amounts of copper to produce six to nine treatments that range from a dose that does not cause toxicity to a dose that causes nearly complete mortality or abnormal development. Data from preliminary tests will be used to select treatment concentrations for Mdr Harbor water. Spiked control water treatments are expected to range from approximately 2 to 30 µg/L.

WER exposures will be initiated within 36 hours of sample collection. Each sample/treatment will be tested using five replicates. For each replicate, approximately 250 *M. galloprovincialis* embryos will be exposed in 10 milliliters (mL) of sample for 48 hours. Subsamples of each treatment will be collected for chemical analysis at the beginning (total and dissolved copper; DOC) and end (dissolved copper) of the exposure period.

Embryos are preserved for examination at the end of the exposure period. The preserved samples are examined using a microscope to determine the numbers of normal and abnormal surviving embryos (Figure 2). The percent of normal embryos is calculated from the count. Levels of key water quality parameters (dissolved oxygen, pH, salinity, and temperature) and control performance will be evaluated to assess test batch acceptability and organism condition.

The test will be considered acceptable if three criteria are met: 1) mean normal development in the controls must be at least 90%; 2) mean survival in the controls must be greater than 50%; and 3) the percent minimum significant difference must be less than 25%. The results of copper reference toxicant tests will be compared to past results to evaluate sensitivity of test organisms (EC50 should be within two standard deviations of laboratory mean).

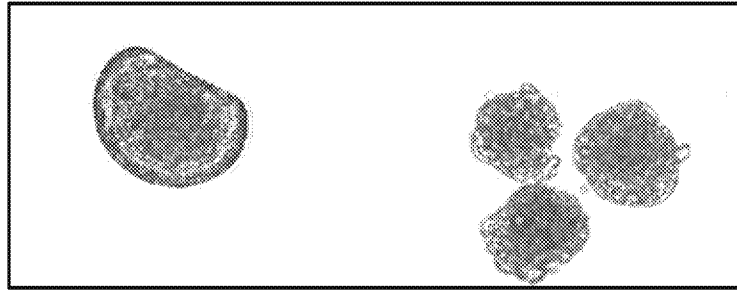


Figure 2. Normally developed (left) and abnormal mussel embryos (images courtesy of Sanitation Districts of Los Angeles County)

Standard statistical methods will be used to calculate the copper EC50 (concentration causing 50% reduction in percent normal-alive) for each sample type. EC50 will be expressed in terms of measured dissolved copper concentration.

Table 1. Summary of test conditions for the 48-hour mussel embryo development test

Test Species	<i>Mytilus galloprovincialis</i>
Test Procedures	USEPA/600/R-95/136
Age/Size Class	Embryo
Endpoint	Normality of development and survival
Test Type/Duration	Acute static non-renewal/48 hours
Sample Storage Conditions	4°C, dark, minimal head space
Holding Time	≤ 36 hours
Control	Filtered natural seawater (from Granite Canyon, California)
Salinity Adjustment	Hypersaline brine
Water Quality Parameters	Temperature 15 ± 1°C
	Dissolved oxygen ≥ 4.0 mg/L
	Salinity 32 ± 2 g/kg
	pH 7.5 to 8.3
Photoperiod	16 hours light, 8 hours dark
Test Chamber	22 mL glass shell vials
Replicates/Sample	5
No. of Organisms/Replicate	250
Exposure Volume	10 ml
Aeration	None
Feeding	None
Water Renewal	None
Reference Toxicant	Copper chloride
Test Acceptability Criteria	Control mean normal development ¹ ≥ 90%
	Control mean survival > 50%
	Percent minimum significant difference < 25%

Notes:

g/kg = grams per kilogram

mg/L = milligrams per liter

mL = milliliters

USEPA = U.S. Environmental Protection Agency

¹ Applied to surviving control embryos

Water-Effect Ratio Study Design

The study design is based on the conceptual approach outlined in the USEPA (1994) Interim Guidance and includes key design elements used in three recent WER studies conducted in California. The USEPA (1994) Interim Guidance recommends that WER analyses be conducted over a range of conditions so that the results are representative of the variations in water quality at the site. The guidance also states that the study should include multiple stations distributed over a minimum of three separate sampling events that include different seasons and locations.

The USEPA (1994) Interim Guidance recommendations have been implemented in different ways in recent California studies. The WER study for San Francisco Bay (north of Dumbarton Bridge) used a study design that was modeled after ongoing regional water quality monitoring programs (Clean Estuary Partnership 2005). Station locations were selected to match those used in other monitoring programs and represent variations in water depth and harbor region. Two sampling events were conducted in each of two seasons: wet and dry. WER analyses conducted in Shelter Island Yacht Basin were based on only two season-specific sampling events: the summer dry season and the winter wet season following a major storm event (Bosse et al. 2014). This study also examined spatial variation by distributing stations along a transect from the head to the mouth of the basin and investigated variation related to depth by collecting samples near the surface and just above the bottom at each station. Among these studies, the size, morphology, and hydrology of the Shelter Island Yacht Basin study site is the most similar to that of MdR Harbor. For the Los Angeles River and tributaries total maximum daily load WER study, a preliminary study design was developed that included six sampling events that were distributed among three seasonal conditions: summer dry weather, winter dry weather, and winter wet weather (Steering Committee 2014). This sampling design was informed by prior studies using the BLM and refined on the basis of initial study results.

5. Station Locations

The station locations for the study are a subset of 11 candidate stations used in previous monitoring surveys (Figure 3). These stations include nine locations used for metals analysis in the MdR Harbor TMDL Coordinated Integrated Monitoring Program (CIMP; Weston 2014), consisting of one station in each of the harbor's eight basins and one station at the end of the main channel (Table 2). Co-location of the stations with the CIMP will increase the comparability of data between the two programs. These stations were augmented by adding two additional main channel stations, located near the harbor entrance and near the mid-point of the channel, which were sampled in 2018 to provide additional site characterization information. These additional stations were included to provide a more complete representation of variations in harbor water quality associated with tidal flushing and internal circulation patterns. These 11 stations represent spatial variations in water quality associated with factors such as urban runoff, boat density, water circulation, and shipyard activities.

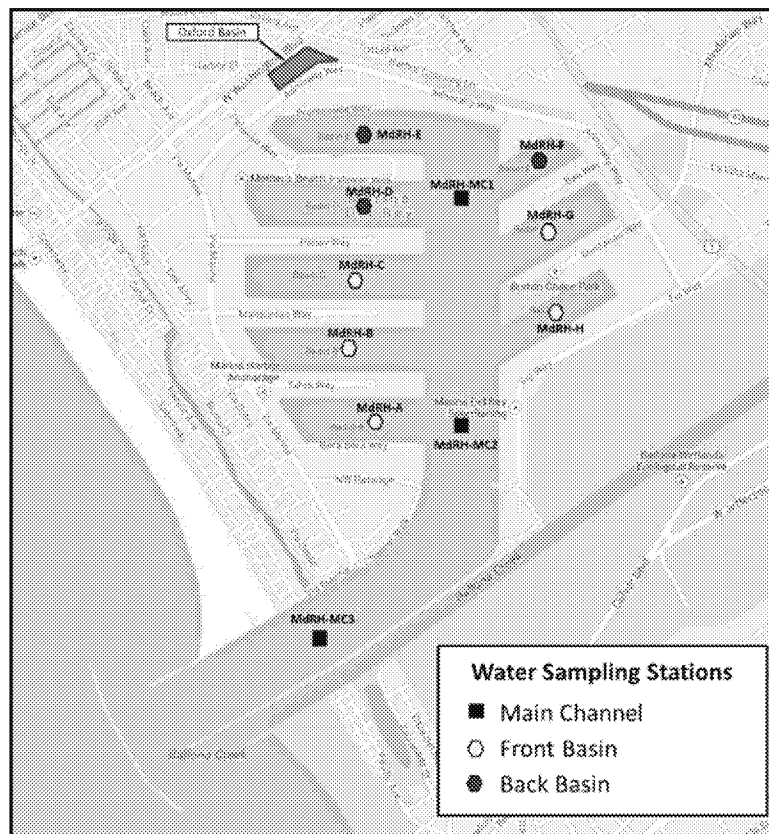


Figure 3. Candidate sampling stations in Marina del Rey Harbor.

Table 2. Station locations

Station ID	Description	Latitude	Longitude
MdRH-MC1	Main Channel, end	33.98054	-118.44819
MdRH-MC2	Main Channel, middle	33.97231	-118.448
MdRH-MC3	Main Channel, entrance	33.96427	-118.455
MdRH-A	Front Basin A, middle	33.97251	-118.45284
MdRH-B	Front Basin B, middle	33.97514	-118.45346
MdRH-C	Front Basin C, middle	33.97773	-118.45372
MdRH-D	Back Basin D, middle	33.98022	-118.45356
MdRH-E	Back Basin E, middle	33.98301	-118.45338
MdRH-F	Back Basin F, middle	33.98198	-118.44502
MdRH-G	Front Basin G, middle	33.97939	-118.44435
MdRH-H	Front Basin H, middle	33.97635	-118.44409

Three water quality surveys were conducted in 2018 to characterize variations in Harbor water quality for parameters affecting copper toxicity (Table 3). One event occurred in March, the day after a rain event resulting in 1.1 inches of precipitation. The other two events (May and September) represented dry weather conditions in the Harbor. Water samples were collected from the surface and near bottom during the first two events, and from the surface only during the third event. Each sample was analyzed for parameters required to apply the BLM model (pH, salinity, temperature, DOC), as well as total and dissolved copper, chlorophyll, and toxicity (mussel embryo development test).

Table 3. Water quality survey events.

Event	Date	Description	Precipitation (in)	Depth ¹
1	3/23/2018	Winter, wet weather	1.1	S, B
2	5/21/2018	Spring, dry weather	0	S, B
3	9/10/2018	Summer, dry weather	0	S

¹ S = Surface; B = Bottom

Variation in dissolved organic carbon (DOC) is the primary factor controlling copper bioavailability in marine systems and is highly correlated with BLM model results. Increased

DOC concentration reduces copper bioavailability and toxicity. Seasonal and spatial variations in DOC were observed among the sampling events (Table 4). Seasonally, DOC was highest on average and more variable during event 1 (wet weather), compared to the two dry weather events. Discharge of stormwater runoff containing high concentrations of organic material to harbor surface water is the likely cause of this pattern. This hypothesis is supported by lower salinity in some surface samples and generally lower DOC concentrations in event 1 bottom water samples (compared to surface samples). Little difference in surface and bottom DOC concentrations was observed during dry weather (event 2).

A spatial pattern in DOC concentration was apparent for each sampling event. The lowest DOC concentrations were always observed at stations in the front basins (A) or in the main channel and close to the harbor mouth (MC3). Locations of the highest DOC were more variable but were frequently located in the back basins of the Harbor. This spatial pattern is likely related to circulation patterns within the Harbor, with low DOC at sites having greatest mixing with offshore water.

Chlorophyll content of the water also varied spatially, with higher concentrations usually present in the back basins. Increases in chlorophyll (a measure of biological productivity) was positively correlated to DOC in Event 2.

Table 4. Water quality survey results for dissolved organic carbon.

Event	Description	Depth	DOC (mg/L)		
			Average	Lowest	Highest
1	Winter, wet weather	S	1.1	0.88 (MC3)	1.41 (A)
1	Winter, wet weather	B	0.94	0.78(MC3)	1.12 (H)
2	Spring, dry weather	S	0.77	0.54 (A)	1.0 (D)
3	Spring, dry weather	B	0.76	0.44 (MC3)	0.95 (MC1)
3	Summer, dry weather	S	0.84	0.74 (MC3)	1.02 (H)

The water quality results indicate that the critical condition, when water quality characteristics provide the greatest relative copper bioavailability, is likely to occur during dry weather in winter or spring, when biological productivity is low and land-based discharges are also low.

Based on the 2018 water quality results, a subset of five stations is recommended for WER analysis (Figure 4). These stations represent locations where DOC concentrations are likely to be lowest (main channel station MC3, and front basins A and B), as well as locations where DOC and copper concentration are likely to be high (back basins E and F). Sampling these stations at multiple times throughout the year is expected to represent variations in water quality factors controlling copper bioavailability throughout the Harbor, as well as encompassing the critical condition during each time.

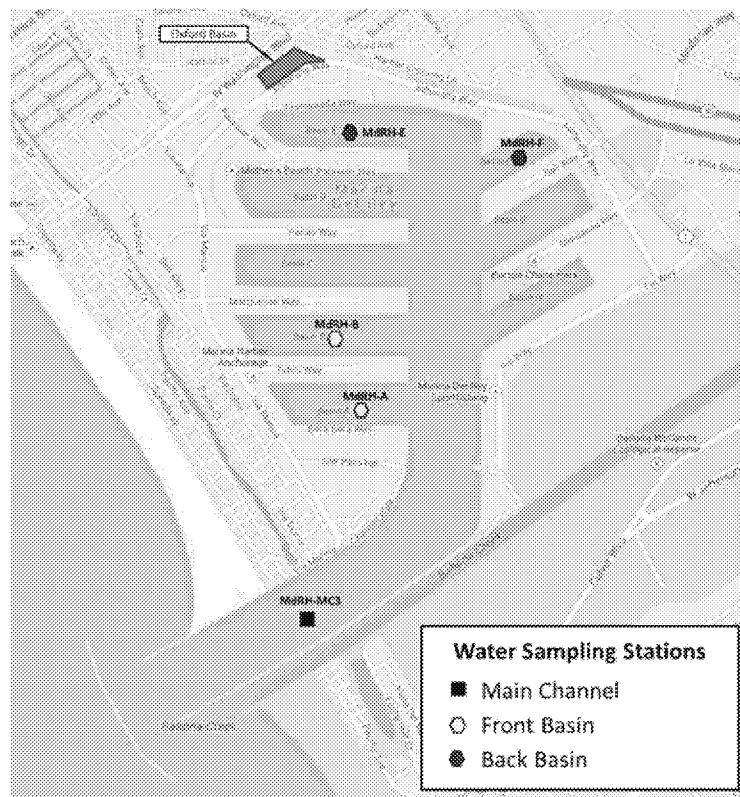


Figure 4. Proposed stations for WER analysis.

6. Sampling Design

Six sampling events are proposed for WER calculation (Table 5). The events will be distributed over an approximately 12-month period to capture major seasonal variations in water quality. Most of the sampling events (4-5) will occur during dry weather, when the critical condition is

expected to be present. The specific time of the sampling will be determined by the tidal cycle. The sampling plan incorporates the three environmental factors expected to have the greatest influence on copper bioavailability: harbor location (e.g., mixing with coastal water), season, and stormwater discharge. The actual number of sampling events conducted may vary, depending on the results of the study.

Table 5. Proposed water-effect ratio sampling events.

Event	Tide Stage		Summer	Winter	
			Dry Weather	Dry Weather	Wet Weather
	Flood	Ebb	April – October	November – March	November – March
1	X		X		
2	X			X	
3		X	X		
4		X		X	
5	NA	NA			X
6	TBD	TBD	TBD	TBD	TBD

Notes:

Wet weather sampling is not dependent on tide stage. Sampling event characteristics to be determined based on results of previous events.

NA = not applicable

TBD = to be determined

The tidal cycle at the time of sampling, whether an incoming (flood) tide or an outgoing (ebb) tide, will affect the degree of mixing of harbor water with offshore coastal water, and thus water characteristics such as dissolved organic carbon concentration. Previous studies in bays have shown that the WER is strongly influenced by the water circulation and degree of mixing with coastal water (Tetra Tech et al. 2000). Variations in both tidal stage and relative change in tide level will be considered in planning the sampling events.

Sampling will be conducted in both summer and winter dry seasons, consistent with the design used in previous WER studies. Variations in temperature, plankton abundance, DOC concentration, and runoff inputs are expected to be associated with these seasons. Two sampling

events are planned for each season, with each event representing a different phase of the tidal cycle.

One sampling event during wet weather (following substantial rainfall) is proposed to confirm preliminary findings that indicate relatively low copper bioavailability during this time. The magnitude of the influence of stormwater discharges on copper bioavailability in MdR Harbor is likely to be variable. Depending on the amount of local precipitation and tides, stormwater enters the harbor via discharge from the Oxford Flood Control Basin to Basin E, from a portion of the Ballona Creek discharge plume that is reflected into the main channel by the breakwater, and from multiple storm drains throughout the harbor complex (Figure 3). The impact of stormwater discharge on the WER can be variable. In the Los Angeles River, wet weather samples were composed mostly of stormwater and the resulting WERs were usually higher than in dry weather (Steering Committee 2014). In Shelter Island Yacht Basin, lower WERs were obtained for the wet weather sampling event (Bosse et al. 2014). For MdR Harbor, at least one sampling event will be conducted shortly after a qualifying rain event to evaluate the influence of wet weather conditions on the WER and ambient toxicity. Qualifying criteria for sampling will include local precipitation of at least 0.2 inch and an antecedent dry period of at least 3 days.

7. Parameters to be Analyzed

Some of the water quality parameters needed for BLM analysis (e.g., pH, temperature, and salinity) will be measured in the field at the time of water sampling (Table 6). These measurements will be obtained using probes. Chlorophyll concentration (an indicator of phytoplankton abundance) will also be measured in the field; this measurement may be helpful in explaining variations in other parameters, such as WER, DOC, or toxicity.

Grab samples of water will be collected at each station for measurement of DOC, metals, and toxicity. Concentrations of both copper and zinc will be measured, as both of these metals may be elevated in harbors and contribute to ambient toxicity. Zinc concentrations in MdR Harbor are not expected to exceed water quality standards but may be a partial contributor to variations Harbor water toxicity. Inclusion of zinc in this study will facilitate a greater capability to interpret the results and determine the risk associated with copper.

Table 6. Analytes for WER study

Analyte	Occasion of Measurement		Analysis Method	Use
	Field	Laboratory		
pH	X		Probe	BLM
Temperature	X		Probe	BLM
Salinity	X		Probe	BLM
Dissolved Organic Carbon		X	Instrument	BLM
Chlorophyll ¹		X	Fluorometer	Water quality
Total Copper		X	ICP/MS	Water quality
Dissolved Copper		X	ICP/MS	Water quality
Total Zinc		X	ICP/MS	Water quality
Dissolved Zinc		X	ICP/MS	Water quality
Toxicity		X	Laboratory Test	Ambient toxicity

Notes:

BLM = Biotic Ligand Model

¹ Chlorophyll samples will be collected and filtered in the field, and the samples will be extracted and analyzed in the laboratory using fluorometry

8. Sample Collection and Processing

Methods for water sample collection and processing are described in Appendix A. Briefly, a peristaltic pump fitted with Teflon-lined tubing will be used to collect water samples and fill plastic bottles specific for each analyte type (Table 7). Samples for measurement of DOC and dissolved metals will be filtered on site within 15 minutes of collection using plastic syringes fitted with 0.45-micron filters. A “clean hands/dirty hands” technique will be employed during sampling and filtering to prevent contamination of the samples. All samples will be placed in dark coolers with wet ice for temporary storage.

Sampling equipment will be pre-cleaned prior to the sampling event. The pump system will be flushed with site water prior to use at each station. A new filter apparatus will be used for each station.

Table 7. Volumes and containers for field samples.

Analysis Type	Volume (mL)	Container Type/Size
Dissolved organic carbon	50	Glass vial
Dissolved metals	50	Polypropylene tube
Total metals	50	Polypropylene tube
Toxicity	1,000	HDPE bottle

Note:
mL = milliliters

9. Documentation of Chain-of-custody

Samples are considered to be in one's custody if they are in the custodian's possession or view or retained in a secured place. The documents used to identify samples and to document possession are chain-of-custody (COC) records and the field form. COC procedures will be used for all samples throughout the collection and analytical process. COC procedures will be initiated during sample collection. A COC record will be provided with each sample group. Each person who has custody of the samples will sign the form to ensure that the samples are not left unattended. COC forms will be signed by the person transferring samples custody. Additional information regarding COC and a copy of the COC form can be found in the Quality Assurance Project Plan (QAPP; Appendix B).

10. Analysis Methods

The methods for chemical analysis of the samples are described in the Appendix B. The methods have been selected to provide reporting limits below the levels expected in MdR Harbor (Table 8). Metal analysis will be conducted according to USEPA Method 1640 for trace elements in water, using inductively coupled plasma mass spectrometry. In this procedure, trace elements are pre-concentrated based on their reductive precipitation by sodium tetrahydroborate; iron and palladium are added to samples to aid co-precipitation of metal borides and to enhance the precipitation of metals coming out in the elemental form.

Table 8. Chemistry and toxicity analysis methods and reporting limits.

Analyte	Method Detection Limit (µg/L)		Reporting Limit (µg/L)		Analysis Method
	Total	Dissolved	Total	Dissolved	
Organic Carbon	NA	50	NA	500	SM 5310B
Copper	0.025	0.15	0.025	0.15	USEPA 1640 – FePd
Zinc	0.025	0.15	0.025	0.15	USEPA 1640 – FePd
Toxicity	NA	NA	NA	NA	USEPA 1995

Notes:

µg/L = micrograms per Liter

NA = not applicable

SM = Standard Method

USEPA = U.S. Environmental Protection Agency

Dissolved organic carbon will be analyzed on filtered samples using Standard Method 5310B (USEPA 415.1) for the analysis of organic carbon by combustion or oxidation. With this method organic carbon in a sample will be converted to carbon dioxide by catalytic combustion or wet chemical oxidation. The carbon dioxide formed can be measured directly by an infrared detector or converted to methane and measured by a flame ionization detector. The amount of carbon dioxide or methane is directly proportional to the concentration of carbonaceous material in the sample.

Ambient toxicity in the water samples will be measured using the 48-hour mussel embryo development test (Section 2.1). Samples will be tested without modification (e.g., no dilution or spiking). MDr Harbor sample toxicity will be compared to the laboratory control (filtered seawater from reference site).

11. Biotic Ligand Model Analyses

The BLM is a chemical speciation model that can be used to predict the adverse effect levels of metals as a function of water chemistry. A freshwater version of the BLM for copper has been developed and approved by the USEPA for use in developing site-specific water quality criteria (Santore et al., 2001). For this study, the draft BLM for copper in saltwater developed by HDR (2012), which is currently under review for publication by the USEPA, will be used.

Application of the BLM requires the input of four water chemistry parameters from the site: salinity, temperature, pH, and DOC. Using chemical speciation data of the different components in seawater, the BLM will be used to predict the $EC_{50\text{BLM}}$; the concentration of dissolved copper needed to produce an adverse effect on 50% of developing mussel embryos in samples of both site water and laboratory control seawater. The predicted EC_{50} values will be used to calculate the BLM predicted WER, defined as the site water $EC_{50\text{BLM}}$ divided by the control water $EC_{50\text{BLM}}$ (see Equation 3 in Section 1.2.2).

12. Sampling Quality Assurance/Quality Control

Multiple quality assurance (QA) samples will be collected and processed in the field. QA samples include travel blanks, field blanks, field duplicates, matrix spikes, and pump tubing blanks (Table 9). One of each QA sample type will be collected during each sampling event. Furthermore, samples of tubes, syringes, filters, and bottles from every new manufacturing lot will be sent to the analytical laboratory for blank analysis.

Table 9. Description of quality assurance sample types for field sampling.

Sample Type	DOC Volume (mL)	Total Metals (mL)	Dissolved Metals (mL)
Travel Blank	50	250	50
Field Blank	50	250	50
Field Duplicate	50	250	50
Matrix Spike Blank	100	250	50
Pump Tubing Blank	0	250	50

Notes:

DOC = dissolved organic carbon

mL = milliliters

Water-Effect Ratio Testing

All water samples will be tested for toxicity and WER calculation using test methods described in Section 2.1. The only substantial difference will be in toxicity test design. A series of spiked copper treatments will be prepared and tested for WER analysis. The spiking methods will follow recommendations in the USEPA (1994) Interim Guidance. Water from each MdR Harbor station and the laboratory control will be spiked to generate a series of copper concentrations designed to produce toxicity results ranging from no effect to complete inhibition of normal embryo development.

Toxicity test results for each copper treatment will be expressed as average percentage normal of five replicate test chambers. Control performance will be compared to test acceptability criteria and water quality specifications (Table 1) to verify data quality.

A subset of the spiked copper treatments for each sample will be analyzed to verify dissolved copper concentrations. Only those treatments used in the statistical analysis to determine the EC50 will be submitted for chemical analysis.

Water-Effect Ratio Analysis and Interpretation

The USEPA (1994) Interim Guidance presents information on calculating and interpreting results. The general steps include:

- Evaluating the acceptability of each toxicity test
- Calculating the results of each test
- Evaluating the acceptability of the laboratory dilution water
- Calculating the sWERs
- Investigating the WER

Completing the first three steps and calculating copper EC50 values for each sample will use methods and criteria in accordance with USEPA (1995). Generally, the EC50 will be determined using the Trimmed Spearman-Kärber method.

The sWER will be calculated as the ratio of the sample EC50 divided by the control EC50 (Section 1.2.1). The BLM predicted sWER will also be calculated for each sample. The predicted sWER is calculated using copper EC50s for the sample and laboratory control predicted by the BLM.

13. Toxicity Quality Assurance/Quality Control

The practices used by the toxicity laboratory to ensure reliable, high-quality results for the tests conducted for this project are described in the QAPP (Appendix B). The objectives for accuracy and precision involve all aspects of the testing process, including:

- Seawater sampling and handling
- Source and condition of test organisms
- Test conditions
- Instrument calibration

- Use of reference toxicants
- Record keeping
- Data evaluation

Concurrent reference toxicant tests will be conducted for each toxicity test batch to verify the sensitivity and health of the test organisms. The reference toxicant EC50 will be compared to a control chart of historical values. Water quality parameters will be monitored to ensure that they fall within prescribed limits; corrective action will be taken if necessary. All limits established for this study meet or exceed those recommended by the USEPA. All data collected or produced from these analyses will be recorded and summarized to become part of the permanent data record for this study.

14. Chemistry Quality Assurance/Quality Control

Detailed descriptions of QA/quality control (QC) procedures and data quality objectives (DQOs) for the chemical analyses of samples for this project are contained in the QAPP (Appendix B) and chemistry laboratory standard operation procedures included with the QAPP. QA/QC involves all testing aspects, including:

- Method SOPs
- Calibration methods and frequency
- Data analysis, validation, and reporting
- Internal QC
- Preventive maintenance
- Procedures to ensure data accuracy and completeness

Laboratory QC results, qualifications, and exceptions will be reported. Laboratory accuracy will be indicated by analysis of matrix spikes, blank spikes, certified reference materials, and/or recovery surrogates. Matrix spikes will be used to assess the effects that the sample matrix (e.g., seawater) has on the accuracy of a measurement. Blank spikes will demonstrate the performance of the preparation method on a clean matrix, void of potential interferences. Precision will be determined by analysis of duplicate matrix spikes, blank spikes, recovery surrogate spikes, and duplicate test samples. Potential laboratory contamination introduced during analysis will be assessed by analyzing procedural/method blanks. Any QC samples that fail to meet the QC criteria detailed in QAPP (Appendix B) will be identified, corrective action taken, and the corresponding data will be appropriately qualified in the final report. All QA/QC records will be kept on file.

15. Water-Effect Ratio Investigation

The sWERs for different stations and events will be summarized and evaluated to determine if the results are sufficient for calculation of the fWER. These analyses will be structured to answer the following questions:

- Do the samples represent typical MdR Harbor conditions?
- Is the critical condition adequately represented?
- Is the sWER sample size and precision sufficient for calculation of the fWER?
- Are the toxicity-based and BLM predicted sWERs comparable?

Water quality (e.g., pH, DOC, temperature, and salinity) and copper concentration measurements for the field samples will be compared to values obtained in prior studies and TMDL monitoring to determine if the samples are representative of MdR Harbor. Statistical evaluation will include comparing sample data to the 95% prediction interval for the parameters.

Representation of the critical condition will be assessed by comparing the season and tide stage of each sampling event to the conditions characteristic of the critical condition. A determination will be made as to whether the goal of conducting four sampling events during the critical condition was met.

The criteria and statistical methods used to evaluate sWER sample size precision will be developed in consultation with the TAC. One potential statistical method is to calculate the size of the 95% prediction interval for the sWER dataset (or region-specific subset) and compare it to the maximum interval size desired.

Three approaches will be used to investigate the comparability of the toxicity-based and BLM predicted sWERs:

1. Summary statistics (e.g., mean, standard deviation, and range) will be compared between the two types of sWER. This analysis will indicate the overall magnitude of differences between the methods.
2. T-tests or ANOVA will be used to determine if mean sWERs are significantly different.
3. Graphical methods (e.g., scatterplots) will be used to compare pairs of individual sWERs matched by station. This analysis will indicate whether there is a pattern of consistent bias between the two WER approaches.

The results of the WER investigations described above will be reviewed to determine if data are sufficient to support fWER calculation at the desired level of precision and seasonal specificity. If not, the feasibility of conducting additional sampling and analyses will be explored.

Final Water-Effect Ratio Calculation

The fWER will be calculated as the geometric mean of the group of sWERs selected for analysis, as recommended in the USEPA (1994) Interim Guidance. The geometric mean is calculated as the average of the natural log-transformed sWERs.

The number and type of fWERs calculated will depend on the characteristics of the sWERs and final study objectives. For example, if statistical analyses indicate that sWERs collected in different regions of the harbor (or different seasons) are similar, then data may be pooled and a single fWER calculated. Alternatively, several fWERs may be calculated to represent important variations in critical condition or copper bioavailability (e.g., front basins vs. back basins).

A determination of the number and type of fWERs to be calculated will be made in consultation with the TAC, Los Angeles RWQCB, and TMDL participants.

III. DATA MANAGEMENT

Data management will involve compiling data collected as part of the SSO study into standardized formats, data review, and export of field, toxicity test, and chemistry data as flat files that are accessible by Los Angeles County Department of Public Works (LACDPW). Data will be reviewed for quality and completeness, compiled, and exported in a standard format to LACDPW.

Analytical Chemistry Data Quality Review and Management

Analytical chemistry data will be submitted by the laboratory in specified PDF and electronic data deliverable formats. Analytical data will undergo verification and validation in accordance with the QAPP (Appendix B) and final validation qualifiers will be applied and stored. A concise data validation summary will be prepared and included in the final report.

Toxicity Test Data Quality Review and Management

All toxicity test data including laboratory bench sheets (listed in the QAPP; Appendix B) will be reviewed to ensure that data meet QA/QC standards specified in the standard method guidance documents. The toxicity test data review process is detailed in the QAPP and briefly described here. A determination will be made as to whether DQOs were met by assessing test acceptability criteria, reference toxicant test results, protocol deviations (i.e., water quality deviations), sample handling notes, and data completeness. Minor data quality issues, that likely do not affect the test outcome, will be noted and summarized in the final report. Database contents will be compared to bench sheets to ensure that the electronic data are complete and accurate.

Data deliverables

A draft Excel database containing data collected during the first half of the SSO study will be provided for review. A final Excel database containing field sampling coordinates, field water quality measurements, compiled validated analytical data, and compiled toxicity summary data for the entire study will be provided along with the final report.

IV. DELIVERABLES AND REPORTING

Task Reports

Interim progress reports and data summaries will be provided as specific study tasks are completed. The format and content of these reports will vary, according to the nature of the activity. Reports for key tasks will include the following:

- Quarterly progress reports covering all activities
- Summary of field sampling events, including station locations and a description of deviations from the sampling plan
- Summary of water chemistry results for each sampling event
- Summary of toxicity results for each testing event
- Summary tables of WER values, BLM output, and predicted WERs
- Data validation summary

Site-specific Objective Study Report

The results of the SSO tasks will be summarized, integrated, and evaluated in a draft report. Laboratory reports, copies of field forms, and data validation reports will be included as appendices. At a minimum, the following will be included in the report:

- Summary of all field activities, including a description of any deviations from the approved work plan
- Locations of stations in latitude and longitude (degrees, decimal minutes)
- Project maps with actual sampling locations
- Summary of water chemistry results compared to CTR criteria
- Summary of toxicity results and WER values
- Conclusions
- Data validation summary

The draft report (two hard copies and an electronic copy) will be prepared for LACDPW review and comment. Following receipt of comments and revisions to the draft report, a draft final report will be prepared for review by the TAC, RWQCB, and other public agencies. All comments will be reviewed and addressed, and a final report will be prepared and provided to LACDPW (three hard copies and an electronic copy).

V. PUBLIC PARTICIPATION PLAN

Public participation will be actively sought during the SSO study. Various stakeholders including non-governmental organizations (NGOs), boaters, marina operators, Harbor lessees,

and other interested parties will be invited to listen in during TAC review meetings, and two public workshops. The first public workshop will be scheduled after the completion of a draft work plan and concurrent with the public work plan review. The second workshop will be scheduled after the completion of a draft final report to explain the outcomes of the SSO study and to solicit comments from the public before the finalizing the final report. All key documents from the SSO study, including the draft work plan, draft final report, and draft implementation strategy report will be available for public review for 30 days once they are submitted to the RWQCB. Public review comments will be considered in preparation of the final documents.

VI. TECHNICAL ADVISORY COMMITTEE

A TAC has been established to provide scientific review and guidance for the SSO study. Three scientists with expertise in metal speciation, bioavailability, toxicology, ecology, and water quality modeling comprise the TAC (Table 10). The TAC members were selected based on recommendations from RWQCB staff and environmental groups. Each of the TAC members have international and national recognition as leaders in their field, extensive publication records, and a mixture of local and international experience. The TAC will provide an independent review of the study design, study results, and final report. The TAC will also provide a resource to questions or concerns from stakeholders that require the application of expert judgment. Additional background on the TAC members is provided in Appendix C.

Table 10. Technical Advisory Committee Members

Name	Affiliation	Expertise
Peter Campbell	University of Quebec, INRS, Quebec, Canada, Emeritus Professor	Trace metal analysis, speciation, toxicology, bioaccumulation
Gary Cherr	Bodega Marine Laboratory, University of California, Davis, Professor	Reproductive physiology, developmental biology, biochemistry, environmental toxicology
Richard Ambrose	Department of Environmental Health Sciences and Institute of the Environment and Sustainability University of California, Los Angeles, Professor	Monitoring and restoration of coastal habitats, especially wetlands; alternatives for managing watershed-level ecological problems resulting from urbanization; evaluating climate change impacts; ecological aspects stormwater treatment

VII. IMPLEMENTATION REPORT

Following the completion of the SSO final report, an implementation report will be developed in coordination with LACDPW and the regulatory agency in order to incorporate the SSO study results in an amendment to the Basin Plan and the Toxics TMDL.

The implementation report will include recalculations of TMDL numeric targets for dissolved copper in MdR Harbor; i.e., chronic CCC and acute CMC will be recalculated using fWERs specific to MdR Harbor. The implementation report will also include recalculation of TMDL load allocation for dissolved copper in MdR Harbor based on the recalculated CCC. In addition, the implementation report will provide analyses to support the implementation of the SSOs for dissolved copper in MdR Harbor including environmental and economic impacts, California Water Code Section 13241, anti-degradation review (as appropriate), and anti-backsliding review (as appropriate).

A draft implementation report (electronic copy) will be submitted to LACDPW and the RWQCB staff for review. All comments will be reviewed and addressed accordingly. A final implementation report will be submitted to the LACDPW (3 hard copies, 1 electronic copy). A copy of the final implementation report will be also submitted to the RWQCB E.O.

VIII.PROJECT SCHEDULE

A project schedule with key milestones has been developed and is provided in Table 11.

Table 11. Site-specific objective study schedule

Deliverables	Target Date¹
Review of work plan by stakeholders	November 2018
TAC Meeting 1: Review of work plan ²	December 2018
TAC Meeting 2: conference call to discuss work plan revisions	January 2019
Submission of revised SSO Work Plan for Los Angeles RWQCB approval	February 2019
Public Outreach Workshop 1: Study background and description of work plan	February 2019
WER Sampling and Testing	February 2019 to February 2020
TAC Meeting 3: conference call to discuss interim results of WER analyses	May 2019
TAC Meeting 4: conference call to discuss interim results of WER analyses	December 2019
TAC Meeting 5: conference call to discuss preliminary WER results	April 2020
SSO Draft Report and Implementation Draft Report	July 2020
TAC Meeting 6: conference call to discuss TAC's review of the draft report	August 2020
TAC Meeting 7: discussion of revised SSO Final Report	September 2020
Public Outreach Workshop 2: Presentation of report findings to stakeholders	October 2020
Final SSO and Implementation Reports	October 2020

Notes:

RWQCB = Regional Water Quality Control Board

SSO = site-specific objective

TAC = Technical Advisory Committee

WER = Water Effect Ratio

¹Dates are for planning purposes only; specific dates for meetings have not yet been established.

²An orientation conference call with the TAC will be held prior to the December meeting.

IX. REFERENCES

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APPENDIX A

SAMPLING AND LABORATORY METHODS

ASSOCIATED LABORATORIES

ASSOCIATED LABORATORIES
806 North Batavia
Orange, CA 92868

TOTAL ORGANIC CARBON
TOC

EPA 415.1 (SM 5310B)

March 2015

DOCUMENT #: G-0001

Filename: SOP TOC, March 2015.doc

I. SCOPE AND APPLICATION:

1. This method measures organic carbon in drinking, surface and saline waters, domestic and industrial wastes.
2. This method is applicable to measurement of organic carbon above 1 mg/L.

II. SUMMARY OF METHOD:

1. The sample is acidified to pH <2 with hydrochloric acid or phosphoric acid, and then purged with purified air to remove carbonate and bicarbonate. After purging, the sample is injected into a heated reaction chamber and packed with an oxidative catalyst such as cobalt oxide. The water is vaporized and the organic carbon is oxidized by CO₂ and H₂O. The CO₂ is transported in the carrier-gas streams and is measured by means of an infrared analyzer.
2. Acidifying samples to pH <2 and purging remove carbonate and bicarbonate, in addition to volatile organic carbon (VOC). In many surface and ground waters the VOC contribution to TOC is negligible. Therefore, in practice the Non-Purgeable Organic Carbon (NPOC) determination is substituted for TOC.

III. DETECTION LIMITS:

1. Detection limits are continuously updated on an annual basis, or more often as needed, and are tracked using a separate system.

IV. DEFINITIONS:

1. Special terms are defined the first time they appear in the text. For additional clarification of terms, refer to USEPA Method 415.1 or Standard Methods (19th Edition), Method 5310B.

V. INTERFERENCES:

1. Volatiles can also be lost during sample blending, particularly if the temperature is allowed to rise.
2. Another significant loss can occur if large carbon-containing particles fail to enter the needle for injection.

VI. SAFETY:

1. Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of chemicals specified in this method. A reference file of Material Safety Data Sheets (MSDS) should be made available to all personnel involved in the chemical analysis.

VII. APAPRATUS AND MATERIALS:

1. Instrument 1: Shimadzu TOC-5000 Analyzer, capable of measuring Total Carbon (TC), Organic Carbon (IC), Total Organic Carbon (TOC), and Non-Purgeable Organic Carbon (NPOC) in water. The measurement system is based on the combustion/non-dispersive infrared gas analysis method widely employed for TOC measurement.
2. Instrument 2: Shimadzu TOC – V.
3. Waring-type blender for homogenizing samples.
4. 0.45 um membrane filters

VIII. SAMPLE COLLECTION, PRESERVATION, & STORAGE:

Total Organic Carbon, TOC

1. Preservative: Hydrochloric Acid or Phosphoric Acid to pH <2.
2. Storage: Cool to 0 – 4 °C.
3. Container: Amber glass bottle with teflon-lined caps, 250 mL.
4. Holding time: 28 days.

Dissolved Organic Carbon, DOC

1. Field filter the sample and then adhere to items 1-4 of the TOC section above
- or
2. Collect the sample unpreserved in an amber container and cool to 4°C. The laboratory will filter and preserve the sample as soon as possible after receipt.

IX. REAGENTS:

1. Reagent Water – Blanks and standards are prepared using water from the nanopure de-ionized type I water system.

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2. Acid – Concentrated Hydrochloric Acid or Phosphoric Acid.
3. Potassium Hydrogen Phthalate, Anhydrous, Primary Standard Grade (PHP) – Dry for one hour at 105 °C before using.
4. NIST Standard: 1000 mg/L.
5. Organic Carbon Stock Solution (1000 mg/L) – Dissolve 0.2125g of PHP in reagent water, adjust to pH <2 and dilute to 100 mL.
6. Carrier Gas – Ultra Zero Pure Air, Liquid Carbonic Product #CA/UZ, Cylinder Size J, Oxygen 18-21%, Total Hydrocarbon <0.1 ppm.
7. Purging Gas – Same supply as the carrier gas.

X. CALIBRATION:

1. Refer to the Procedure section below for details on calibration.

XI. PROCEDURE:

Total Organic Carbon, TOC

1. If a sample contains gross particulates or insoluble matter, homogenize until a representative portion can be withdrawn through the autosampler needle.
2. Transfer the sample to a 40 mL autosampler vial.
3. Check the sample pH. If it is not already at a pH of 2 or less, add concentrated hydrochloric acid to reduce the pH to a value of 2 or less.
4. Add the sample vial to the instrument autosampler and begin the instrument analysis.
5. Calculations are performed automatically by the instrument.

Dissolved Organic Carbon, DOC

1. Transfer the field filtered and preserved sample to a 40 mL autosampler vial. If the sample was not field filtered, rinse a 0.45 um filter with reagent water and filter the sample, discarding the first several milliliters, into a 40 mL autosampler vial, then add concentrated hydrochloric acid drop wise until the pH is 2 or less.
2. Add the sample vial to the instrument autosampler and begin the instrument analysis.
3. Calculations are performed automatically by the instrument.

Instrument Calibration

1. Preparation of Standard Curves – Prepare standard organic carbon curves by diluting stock solutions in the range of 0 to 100 mg/L. Inject and record peak height or area of these standards and a water blank. Inject three to five times for each standard to give a low coefficient of variance. The standard curve is not corrected through the zero point for the blank water contribution. Each curve must have a linear regression value of 0.995 to be in control.

For Instrument 1:

STANDARD CURVE REQUIREMENTS

Curve 1 0.5mg/L to 5mg/L	0.5mg/L	0.5 ml of 1000mg/L NIST standard in 1000ml DI water
	1.0 mg/L	0.5 ml of 1000mg/L NIST standard in 500ml DI water
	2.5mg/L	0.5 ml of 1000mg/L NIST standard in 200ml DI water
	5.0mg/L	0.5 ml of 1000mg/L NIST standard in 100ml DI water
Curve 2 5mg/L to 50mg/L	5.0mg/L	Same as for Curve 1
	10.0mg/L	5.0 ml of 1000mg/L NIST standard in 500ml DI water
	25.0mg/L	5.0 ml of 1000mg/L NIST standard in 200ml DI water
	50.0mg/L	5.0 ml of 1000mg/L NIST standard in 100ml DI water
Curve 3 50mg/L to 100mg/L	50.0mg/L	Same as for Curve 2
	75.0mg/L	7.5 ml of 1000mg/L NIST standard in 100ml DI water
	100.0mg/L	10.0 ml of 1000mg/L NIST standard in 100ml DI water

For Instrument 2:

STANDARD CURVE REQUIREMENTS

Curve 1 0.5mg/L to 5mg/L	Working Standard 10mg/L (1ml of 1000 mg/L NIST standard into 100ml DI water), Auto Dilution: 0.5mg/L(20DF), 1.0mg/L(10DF), 2.5mg/L(4DF) and 5.0mg/L(2DF)
Curve 2 5mg/L to 50mg/L	Working Standard 50mg/L (5.0 ml of 1000mg/L NIST standard into 100 ml DI water, Auto Dilution: 5mg/L(10DF), 10mg/L(5DF), 25mg/L(2DF) and 50mg/L(1DF)

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2. Reference Standard (LCS – 1000 ppm PHP): 0.2125 grams of PHP into a 100 ml volumetric flask with de-ionized water to a pH<2. This standard must be from another source than the standard calibration curve and the data must fall within 15% RPD.

3. Instrument Conditions:

- 3.1. Curve 1:

- 3.1.1. Range = 1
 - 3.1.2. Injection size = 80 ul.
 - 3.1.3. Washes = 4
 - 3.1.4. Sparge Time = 3 minutes
 - 3.1.5. Shift to Origin = No
 - 3.1.6. Number of Injections = 2
 - 3.1.7. Maximum Number of Injections = 3
 - 3.1.8. Curve Type = TC
 - 3.1.9. Standard Deviation = 200
 - 3.1.10. Coefficient of Variance = 1.0%

- 3.2. Curve 2:

- 3.2.1. Range = 5
 - 3.2.2. Injection Size = 50 ul
 - 3.2.3. Washes = 4
 - 3.2.4. Sparge Time = 3 minutes
 - 3.2.5. Shift to Origin = No

- 3.3. Curve 3:

- 3.3.1. Range = 5
 - 3.3.2. Injection Size = 50 ul
 - 3.3.3. Washes = 4
 - 3.3.4. Sparge Time = 3 minutes
 - 3.3.5. Shift to Origin = No

4. General Conditions:

- 4.1. TC Catalyst = High Sensitivity.
 - 4.2. Syringe Size = 250 ul Hamilton.
 - 4.3. Number of Washes = 4 times.
 - 4.4. Units of Concentration = milligrams/liter.
 - 4.5. Auto ranging + injection volume = Off.
 - 4.6. Auto regeneration of IC solution = On
 - 4.7. Auto Printout = data + peak plot.
 - 4.8. TC Furnace = On.
 - 4.9. Buzzer = Off.
 - 4.10. Injection Speed = Standard.
 - 4.11. Syringe Wash (ul) = Standard.

5. Monitor:

- 5.1. TC Furnace Temperature = 680 °C.

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- 5.2. Dehumidifier Temperature = 1.1 °C
- 5.3. Baseline Position = Zero.
- 5.4. Gas = Ultrazero Air, 21% Oxygen, 79% Nitrogen.
- 5.5. Gas Flow = 150 ml/min.
- 5.6. Gas Pressure = 4.5 kg/cm²
- 5.7. Sparge gas flow = 50 ml/min.

6. Autosampler Conditions:

- 6.1. Rinse = Yes.
- 6.2. Number of Needle Washes = 3
- 6.3. Flow line washes = 4.
- 6.4. Calibrate Before = Each sample group.
- 6.5. Print Information = cal + data
- 6.6. Auto addition of acid = off
- 6.7. Acid volume = Zero.
- 6.8. Rinse after addition = no rinse.
- 6.9. Key lock = unlock.
- 6.10. Finish or running:
 - 6.10.1. = No change = run during day.
 - 6.10.2. = 2 = running (turns off gas supply after the run is finished and turns off the furnace and it will turn the furnace back on the date you specify).

7. Gas Supply:

- 7.1. Carrier gas cylinder set at rate of 85 psi.
- 7.2. Carrier gas pressure controller knob is 4.5 kg/cm².
- 7.3. Carrier gas mass flow rotometer is 150 ml/min. Do not change this controller knob after standardization. To change the flow, use gas flow adjustment at the cylinder.
- 7.4. Confirm that carrier gas is supplied before turning on the furnace to prevent "lifting up" of the high sensitivity catalyst in the combustion tube.

- 8. Dehumidifier Drain Vessel – Maintain water level to the level of the drain outlet, the upper opening on the wall of the vessel. If the baseline is erratic and drifting off the zero position, then an empty or low dehumidifier may be the cause of the problem.
- 9. Humidifier – Fill the humidifier with 0.3 N NaOH. Weigh 0.9 grams of NaOH into 75 ml of de-ionized water.
- 10. Catalyst Regeneration – The catalyst must be regenerated when the baseline appears to be erratic or when the baseline does not go back to the zero point easily. The regeneration is done on the maintenance screen and the solution used to regenerate is a 2 N Hydrochloric Acid solution.

XII. CALCULATIONS:

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1. Calculations are performed by the TOC Analyzer.

XIII. QUALITY CONTROL (Including data assessment and acceptance criteria for QC measures & corrective actions and contingencies for unacceptable data):

1. Method Blanks (MB), Laboratory Control Sample (LCS), Matrix Spike and Matrix Spike Duplicates (MS/MSD) are analyzed with each batch of maximum 20 samples.
2. Method Blank (MB)
 - 2.1. QC limits: Less than 0.5 mg/L TOC.
3. Laboratory Control Sample (LCS):
 - 3.1. The LCS spiking solution must be from a second source.
 - 3.2. QC limits: 80-120% recovery.
 - 3.3. If recovery is outside limits, locate and correct the source of the problem, and repeat the test until the limits are met.
4. Matrix Spike / Matrix Spike Duplicate (MS/MSD):
 - 4.1. QC limits: 75-125% recovery.
 - 4.2. RPD limits: 20% maximum.
 - 4.3. If the recovery is outside the limits, but the LCS recovery is acceptable, there is possibly a matrix interference.
5. Initial and Continuing Calibration Verification (ICV/CCV)
 - 5.1. QC limits: 90-110%
6. Initial and Continuing Calibration Blank (ICB/CCB)
 - 6.1. QC limits: Less than 0.5mg/L TOC

XIV. METHOD PERFORMANCE:

1. Method performance is monitored on a continuous basis through the use of Laboratory Control Samples, Method Blanks, Matrix Spikes, and Sample Duplicates.

XV. POLLUTION PREVENTION:

1. The EPA has established guidelines of environmental management techniques to institute pollution prevention in the workplace. Whenever feasible, laboratory personnel use pollution prevention techniques to address their waste generation and minimize pollution resulting from any laboratory activity.

XVI. WASTE MANAGEMENT:

1. Hazardous wastes generated are properly disposed of in accordance to existing federal

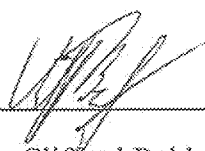
and state regulations.

XVII. REFERENCES:

1. Methods for Chemical Analysis of Water and Wastes. EPA 600 / 4-79-020, revised March 1983 – Method 415.1.
2. Standard Methods for the Examination of Water and Wastewater, 18th Edition.

XVIII. APPROVAL SIGNATURES:

Approved by:



Clifford Baldrige



Dat Phan

Title:

Inorganic Manager

QA/QC Officer

Date:

3/24/15

3.24.15



STANDARD OPERATING PROCEDURE

for EPA Method 1640

**DETERMINATION OF TRACE ELEMENTS IN SALINE WATER BY PRECONCENTRATION
AND INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY**

REVISION # 1 Effective date: June 15, 2010

Approved by:

Name	Title	Phone	Signatures	Date
Misty Mercier	Laboratory Director			
Rhonda Moeller	Quality Manager			